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### Liquid Chromatographic Analysis of Styrene-Methacrylate and Styrene-Acrylate Copolymers

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## LIQUID CHROMATOGRAPHIC ANALYSIS OF STYRENE-METHACRYLATE AND STYRENE-ACRYLATE COPOLYMERS

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### ABSTRACT

Copolymers of styrene-methacrylate (methyl-, ethyl-, and n-butyl-) and styrene-acrylate (methyl-, ethyl-, and n-butyl-) were prepared by solution polymerization at a low degree of conversion. These copolymers were separated according to composition by liquid adsorption chromatography. Silica gel was the stationary phase and a mixture of chloroform and ethanol was the mobile phase. Ethanol content in the mobile phase affected the elution of the copolymers and methacrylate or acrylate rich copolymers required much ethanol to elute from a column. The retention of the copolymers was controlled by column temperature and the copolymers tended to retain in a column at higher column temperature. A linear gradient elution method way to increase ethanol in the mobile phase was effective to separate the copolymers in the order of increasing the methacrylate or acrylate content. Styrene rich copolymers eluted first from a column. Resolution between two adjacent peaks was improved with the increase in column temperature. In a mixture of copolymers of styrene-methacrylate or styrene-acrylate (methyl, ethyl, and n-butyl) having the same styrene content, the elution was in the order of n-butyl, ethyl, and methyl methacrylate or acrylate copolymers with styrene. In

copolymers having the same styrene content, a mixture of copolymers having different ester groups was separated and a mixture of copolymers having the same ester group (e.g., styrene-methyl methacrylate and styrene-methyl acrylate copolymers) was not separated.

### INTRODUCTION

Synthetic random copolymers usually have a molecular weight distribution (MWD) and a chemical composition distribution (CCD). To obtain both MWD and CCD for copolymers, the determination of MWD independently of composition, followed by the separation of the copolymers by composition independently of molecular weight is required. This is the principle of cross-fractionation, which can be performed by means of a combination of several chromatographic methods.

Size exclusion chromatography (SEC) is used for the separation of copolymers according to molecular size. Recent developments in high performance liquid chromatography (HPLC) such as reversed-phase chromatography and adsorption chromatography have enabled the separation of copolymers according to chemical composition. A combination of two separation modes in HPLC, size-exclusion and reversed-phase or adsorption, may be possible to obtain both MWD and CCD for copolymers. Styrene-methyl acrylate copolymers were separated on a system of silica gel/carbon tetrachloride-methyl acetate where carbon tetrachloride was solvent for the copolymers and methyl acetate was non-solvent[1]. A mixture of dichloroethane and tetrahydrofuran (THF) was used for the separation of styrene-methyl methacrylate copolymers[2]. Both solvents were good solvents for the copolymers. Styrene-acrylonitrile copolymers[3] and styrene-methyl methacrylate copolymers[4] were separated by precipitation liquid chromatography. A mixture of n-octane and THF was used as the mobile phase and silica-ODS as the stationary phase. Copolymers which were in-

jected on the inlet of the column were first precipitated on the silica-ODS using the n-octane rich mobile phase and then the content of THF was increased so as to redissolve the precipitated copolymers. Styrene-butadiene copolymers were separated on a system of polyacrylonitrile gel/chloroform-n-hexane[5].

In previous papers, separation of styrene-methyl methacrylate random copolymers according to chemical composition by liquid adsorption chromatography (LAC) has been reported[6-10]. A system of silica gel/chloroform-ethanol has been used and maximum ethanol content was 4.5%. Retention mechanism for the copolymers was considered to be hydrogen bonding between carbonyl groups of the copolymers and silanol groups on the silica surface and not to the solubility difference of the mobile phase to the copolymers. The extent of hydrogen bonding was controlled by the number of silanol groups on the silica surface which was regulated by the ethanol content in the mobile phase, and by the number of carbonyl groups of the copolymers which corresponded to composition of the copolymers. The copolymers containing more styrene eluted earlier from a column. Molecular weight dependence on the separation of the copolymers by LAC was not observed.

In the present work, low-conversion random copolymers of styrene-methacrylate and styrene-acrylate were prepared and the LAC technique used in the previous papers was applied to the separation of the copolymers according to composition.

#### EXPERIMENTAL

Styrene monomer was copolymerized with one of comonomers of methyl methacrylate (MMA), ethyl methacrylate (EMA), n-butyl methacrylate (BMA), methyl acrylate (MA), ethyl acrylate (EA), and n-butyl acrylate (BA) by solution polymerization at a low degree of conversion in benzene at 60 °C for 10 h under nitrogen atmosphere.

TABLE 1  
Composition of the Copolymers used in this Experiment

Sample	Composition, styrene, mol%	Sample	Composition, styrene, mol%
S-MMA I	64.5	S-MA I	65.7
II	47.3	II	51.3
III	28.7	III	35.6
IV	14.7	IV	19.0
S-EMA I	69.1	S-EA I	68.6
II	50.2	II	52.6
III	30.4	III	36.7
IV	15.5	IV	20.7
S-BMA I	69.6	S-BA I	75.5
II	50.3	II	59.2
III	30.7	III	41.0
IV	14.5	IV	15.8

Composition of the copolymers was measured by ultraviolet spectrophotometry at wavelength of 260 nm. A calibration curve was constructed with a polystyrene homopolymer. Composition of the copolymers is listed in Table 1.

LAC was performed on a high performance liquid chromatograph Model TRIROTAR-VI (Japan Spectroscopic Co., Ltd., Hachioji, Tokyo 192) with an ultraviolet detector Model UVIDECE-100VI operated at 254 nm. The column was 50 mm in length and 4.6 mm i.d. and was packed with silica gel of 30 Å pore size and a particle diameter of 5 µm (Nomura Chemical Co., Seto, Aichi 489, Japan). This column was thermostated at a specified temperature in a column oven.

The mobile phase was a mixture of chloroform and ethanol. Elution was performed by both isocratic and gradient elution modes. An isocratic elution mode was applied to investigate the elution behavior of the copolymers by changing the content of ethanol in the mobile phase and by changing column temperature.

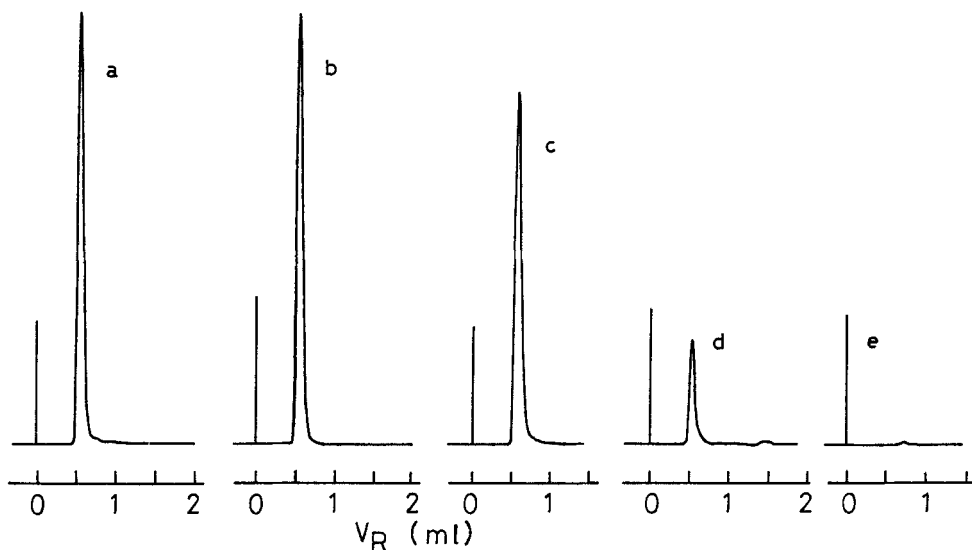


FIGURE 1. Effect of column temperature on the elution of copolymer S-BA II. Column temperature: (a) 30 °C, (b) 40 °C, (c) 50 °C, (d) 60 °C, (e) 70 °C.

Linear gradient elution was applied to separate a mixture of the copolymers according to composition. The composition of the mobile phase was regulated by linear gradient elution as follows: the initial mobile phase (A) was a mixture of chloroform and ethanol (99.0/1.0, v/v), the final mobile phase (B) was chloroform and ethanol (93.0/7.0), and the composition of the mobile phase was changed from 100%A to 100%B in 30 min. The flow rate was 0.5 mL/min. Samples were dissolved in the initial mobile phase in a concentration of 0.1% and sample solutions were injected 1 min after the start of the gradient elution. Injection volume was 0.1 mL.

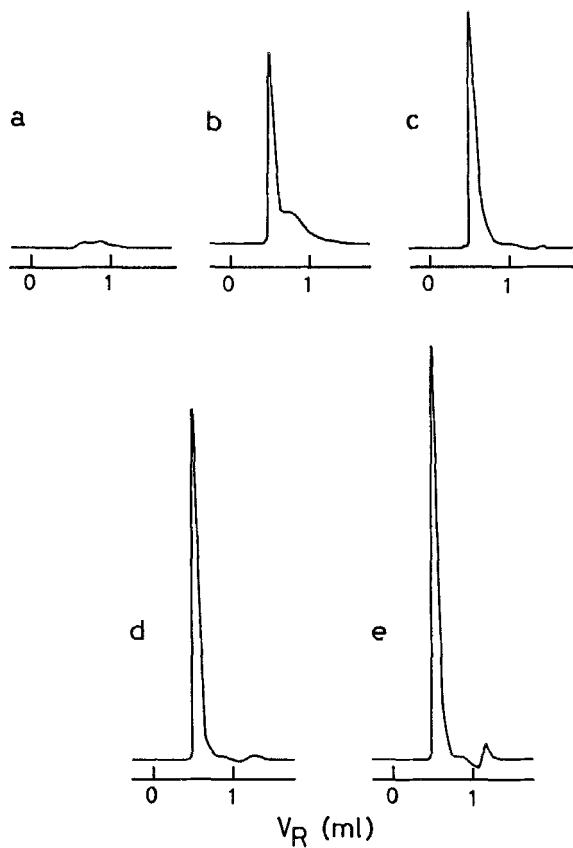


FIGURE 2. Effect of ethanol content in the mobile phase on the elution of copolymer S-EMA II at column temperature 50°C. Mobile phase: chloroform/ethanol, v/v; (a) 99/1, (b) 98/2, (c) 97/3, (d) 96/4, (e) 95/5.

#### RESULTS AND DISCUSSION

Column temperature and ethanol content in the mobile phase affected the retention of S-MMA copolymers[7]. Similarly to the previous results, the elution of styrene copolymers with acrylates and methacrylates from the column was controlled by both factors.

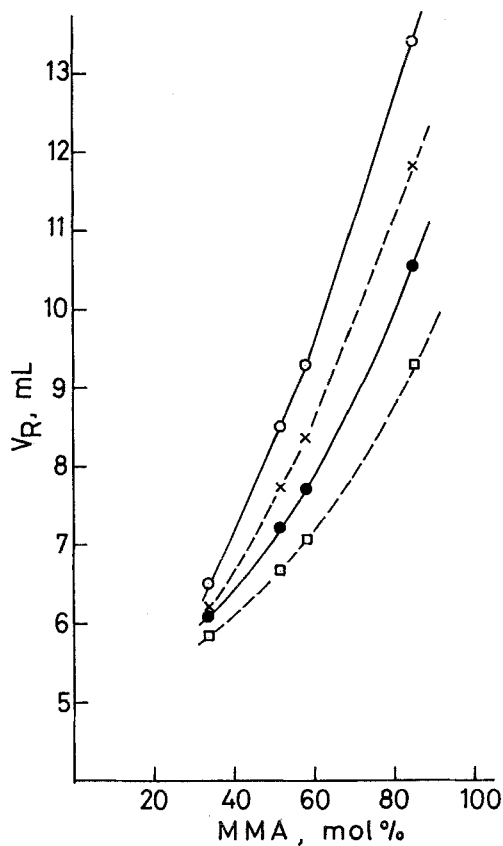


FIGURE 3. Plots of MMA content vs retention volume for copolymers S-MMA at different column temperature. (o) 70 °C, (x) 60 °C, (●) 50 °C, (□) 40 °C.

The copolymers tended to retain in the column at higher column temperatures. Examples are shown in Figures 1 and 2.

At constant composition of the mobile phase (chloroform/ethanol, 99.0/1.0, v/v), elution behavior of the copolymers was investigated by changing column temperature. Examples for chromatograms are shown in Figure 1 for copolymer S-BA II. It eluted



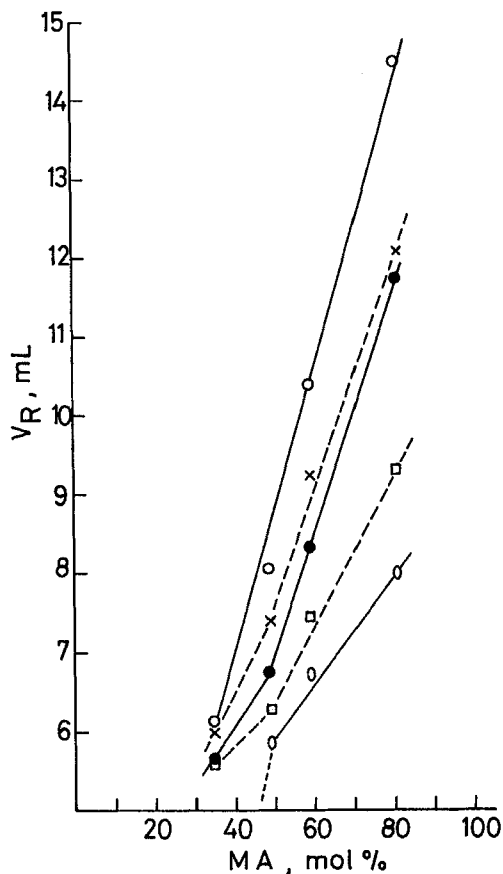


FIGURE 4. Plots of MA content vs retention volume for copolymers S-MA at different column temperature. (o) 70 °C, (x) 60 °C, (●) 50 °C, (□) 40 °C, (○) 30 °C.

100% from the column at column temperatures 30 °C and 40 °C. Peak height at 50°C decreased to 80% of that at 30°C and that at 60 °C to 24%. All the sample copolymers were retained in the column at column temperature 70 °C. Peak retention volume was unchanged with column temperature and it corresponded to the interstitial volume of the column system.

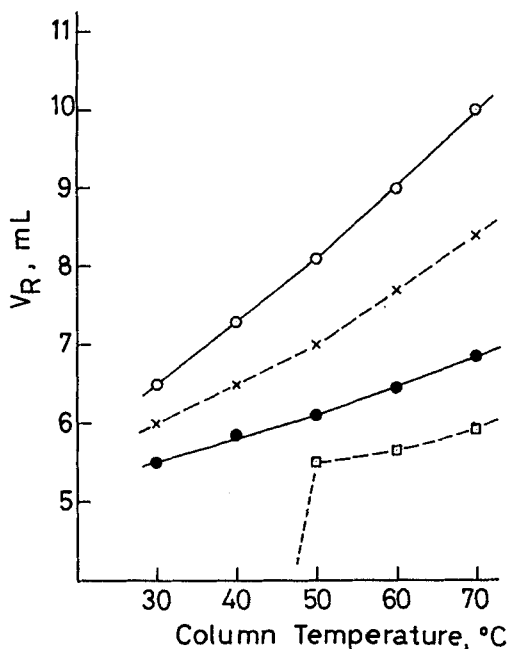


FIGURE 5. Plots of column temperature vs retention volume for copolymers S-EA. Copolymer: (□) S-EA I, (●) II, (x) III, (o) IV.

The mobile phase containing less ethanol in chloroform retains the copolymers in the column. Examples are shown in Figure 2. At column temperature 50 °C, copolymer S-EMA II was retained in the column when chloroform containing less than 1% of ethanol was used as the mobile phase (Figure 2,a). Percentage of the elution of the copolymer by increasing ethanol content in chloroform was as follows: 47% elution at 2% ethanol in chloroform (b), 57% at 3% (c), 85% at 4% (d), and 100% at 5% (e).

The portion of the copolymer retaining in the column contains less styrene than that eluted from the column. Copolymers having less styrene component required a lower column temperature and a higher ethanol content in the mobile phase for the elution from

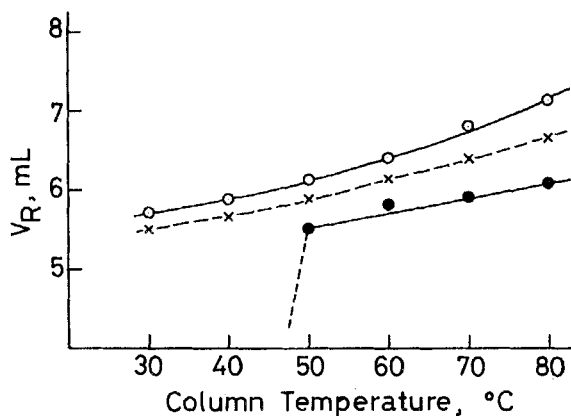


FIGURE 6. Plots of column temperature vs retention volume for copolymers S-BA. Copolymer: (□) S-BA I, (●) II, (x) III, (o) IV.

the column. Copolymers always appeared at the interstitial volume of the column system when they could elute from the column, or they retained in the column.

To separate the copolymers according to composition, gradient elution should be applied as in the previous work[7,8,10]. The copolymers were first adsorbed on the surface of silica gel and then were desorbed in the order of decreasing the styrene content in the copolymers by increasing the ethanol content in the mobile phase. The copolymers, which were not adsorbed on the silica surface, appeared at the interstitial volume in the column system.

Relationships between copolymer composition and retention volume at different column temperature obtained by gradient elution are shown in Figures 3 and 4 for copolymers S-MMA and S-MA. Retention volume increased with increasing ester content in the copolymers and with increasing column temperature. Retention volume difference increased with increasing ester content (decreasing styrene content). Copolymer S-MA I eluted at the interstitial volume at column temperature 30 °C. The relationship for

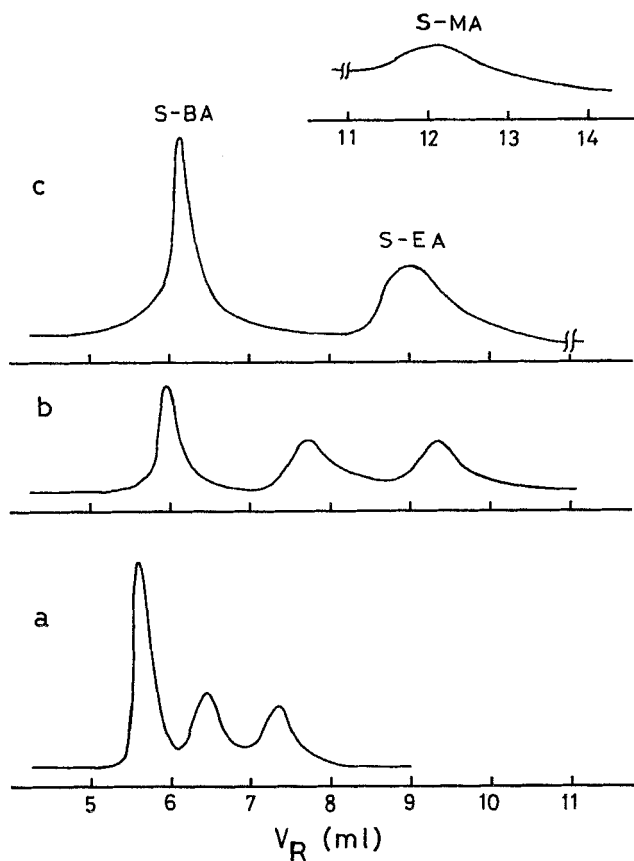


FIGURE 7. LAC chromatograms of mixtures of styrene-acrylate copolymers. (a) S-BA II, S-EA II, and S-MA II, (b) S-BA III, S-EA III, and S-MA III, (c) S-BA IV, S-EA IV, and S-MA IV. Column temperature: 60 °C, UV: 0.16 AUFS.

other copolymers was also determined and similar results have been obtained.

Plots of the above relationship for the copolymers of styrene-methacrylate and styrene-acrylate having the same ester group lay roughly on the same line and a pair of the copolymers having the same ester group and the same styrene content was not separated.

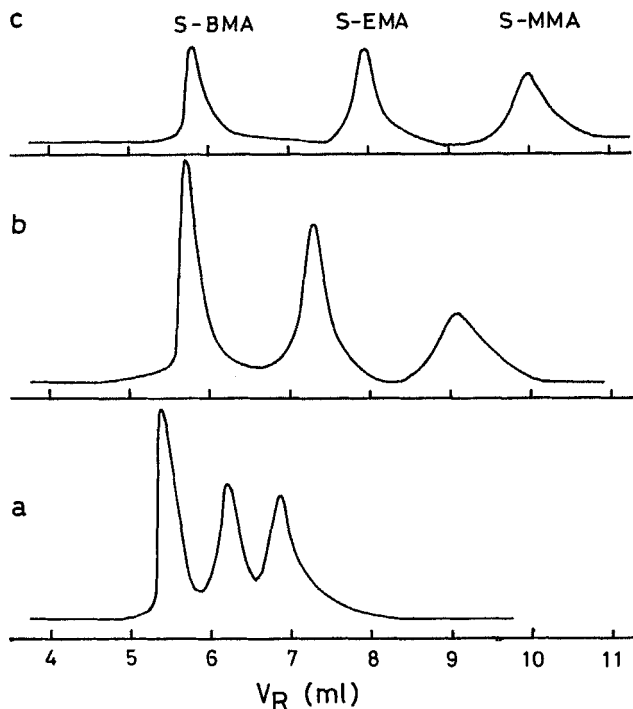


FIGURE 8. LAC chromatograms of mixtures of styrene-methacrylate copolymers. (a) S-BMA II, S-EMA II, and S-MMA II, (b) S-BMA III, S-EMA III, and S-MMA III, (c) S-BMA IV, S-EMA IV, S-MMA IV. Column temperature: 50 °C. UV: 0.16 AUFS.

On the other hand, the copolymers having the same styrene content and the different ester groups were separated and the elution was in the order of styrene copolymers of *n*-butyl, ethyl, and methyl esters. These phenomena will be discussed at the later section. Copolymers having less styrene eluted later from the column.

Column temperature affected the elution of the copolymers. Retention volume of the copolymers decreased with decreasing column temperature. Figures 5 and 6 show the plot of column temperature and retention volume for copolymers of S-EA and S-BA, re-

spectively. Retention volume difference between two copolymers of different composition increased at higher column temperature. Copolymers S-EA I and S-BA I eluted at the interstitial volume at column temperature below 40 °C.

Separation of a mixture of styrene-acrylate copolymers or styrene-methacrylate copolymers having the same styrene content was performed and the results are shown in Figures 7 and 8, respectively. Figure 7 is LAC chromatograms of styrene-acrylate copolymers at column temperature 60 °C. Gradient elution condition was the same at all experiments. Separation was complete in these mixtures. The elution of these copolymers was in the order of S-BA, S-EA, and S-MA copolymers. For a mixture of S-MA IV, S-EA IV, and S-BA IV, column temperature may be lowered to 50 °C or 40 °C to reduce retention volume without loss of resolution.

Figure 8 is LAC chromatograms of styrene-methacrylate copolymers at column temperature 50 °C. The elution was in the order of S-BMA, S-EMA, and S-MMA copolymers. In the case of a mixture of S-MMA II, S-EMA II, and S-BMA II copolymers, column temperature should be raised to 60 °C to improve resolution.

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